Exhibit A

YOR9200303OO

Disclosure YOR8-2003-0325

Prepared for and/or by an IBM Attorney - IBM Confidential

Created By Dinkar Singh On
Last Modified By Dinkar Singh On

Required fields are marked with the asterisk (*) and must be filled in to complete the form.

***Title of disclosure (in English)**
Carbon nanotube diameter control using gas flow

Summary

Status		Under Evaluation
Final Deadline		
Final Deadline Reason		
*Processing Location		Yorktown
*Functional Area	select	(702F) 702F NANOSCALE MATERIALS & DEVICES
Attorney/Patent Professional		Robert M Trepp/Watson/IBM
IDT Team	select	Christopher B Murray/Watson/IBM H-S Philip Wong/Watson/IBM Robert M Trepp/Watson/IBM
Submitted Date		
*Owning Division	select	RES
Incentive Program		
Lab		
*Technology Code		101Y2
PVT Score		

Inventors with a Blue Pages entry

Inventors: Dinkar Singh/Watson/IBM, Deborah Neumayer/Watson/IBM

Inventor Name	Inventor Serial	Div/Dept	Inventor Phone	Manager Name
> Singh, Dinkar V. (Singh)	4A8564	22/K4WC	862-3525	Grill, Alfred
Neumayer, Deborah A.	660407	22/K4WC	862-2601	Grill, Alfred

> denotes primary contact

Inventors without a Blue Pages entry

IDT Selection

Attorney/Patent Professional	Robert M Trepp/Watson/IBM
IDT Team	Christopher B Murray/Watson/IBM H-S Philip Wong/Watson/IBM Robert M Trepp/Watson/IBM

Response Due to IP&L

***Main Idea**

1. Background: What is the problem solved by your invention? Describe known solutions to this problem (if any). What are the drawbacks of such known solutions, or why is an additional solution required? Cite any relevant technical documents or references.

Carbon nanotube based field effect transistors (CNTFETs) show great promise for device applications. The electrical characteristics of CNTFETs however depends strongly on the band-gap of the single wall carbon nanotube (SWCNT) forming the channel of the transistor. Since the band-gap of SWCNTs has a strong dependence on the diameter, accurate control of the diameter is essential to the success of any device technology based on carbon nanotubes. It has been theorized that the particle size of the growth catalyst used can define the diameter of as grown carbon nanotubes. This hypothesis has been supported by the observation that catalytic particles at the ends of CVD grown SWNT have sizes commensurate with the nanotube diameters. Catalysts typically employed are transition metals notably Fe, Co, Mo which agglomerate at the temperatures involved in the growth of carbon nanotubes. Hence a crucial difficulty in obtaining individual SWNTs by CVD is control of nanometric catalyst particle size at growth temperatures of 700-1000 °C. One strategy to control catalyst particle size is to embed them in a high surface area silica or aluminasilicate matrix to limit agglomeration at the high growth temperatures involved. However this approach results in large amount of catalyst residue giving rise to process integration issues. Other approaches to control catalyst particle size include the preparation of dilute discrete nano particles in solution utilizing ferritin (an iron storage protein), micelles, polymers or other coordinating reagents that bind the surface of the nanoparticles and prevent them from growing bigger. However the methods described above result in complicated catalyst preparation and a distribution of catalyst particle sizes which is very difficult to control.

While catalyst particle size seems to play a crucial role in determining the diameter of CNTs, we have recently found that the tube diameter can be controlled using gas flows.

2. Summary of Invention: Briefly describe the core idea of your invention (saving the details for questions #3 below). Describe the advantage(s) of using your invention instead of the known solutions described above.

Control of carbon nanotube diameter using gas flows. While catalyst particle size seems to play a crucial role in determining the diameter of CNTs, we have found that it is possible to control the tube diameter using gas flows.

The possibility of controlling the carbon nanotube diameter by gas flow rather than catalyst particle size, relaxes constraints on the distribution of the catalyst particle size and simplifies catalyst preparation. A strategy which has an advantage in integration of SWNT devices is the preparation of catalyst from thin metal films which ball up during thermal treatment to form nanometric catalyst particles. Thin films of Fe, Co, Ni etc can be easily deposited and precisely patterned using conventional processing techniques. Although this approach provides limited control of the catalyst particle size, the possibility of controlling the CNT diameter by gas flows makes this a very attractive approach.

3. Description: Describe how your invention works, and how it could be implemented, using text, diagrams and flow charts as appropriate.

By varying the gas flow or the pressure in the CVD reactor used for carbon nanotube growth we can accurately control the residence time of the carbon containing gas precursor. As shown in Fig. 1 we can vary the carbon nanotube diameter by almost an order of magnitude, independent of catalyst particle size and growth temperature, by varying the residence time of the carbon containing gas precursor. In the limiting case of high residence time, r the tube diameter is controlled by the catalyst particle size, however as the residence time is decreased tubes with much smaller diameters can be obtained.

fig1.doc

***Patent Value Tool**

* 1. Select the single most appropriate technology category for your invention from the following technologies list.
(101Y2) PPM 100 Solid State Technologies-101Y2 - Nanotechnology: devices(nanotubes, nanowires, nanoparticles etc.) and processes/materials for making these
Comments
Are there any additional significant markets where the invention is likely to have impact?
● Yes ○ No

Please identify them:
Any market involving products that use carbon nanotubes e.g. field emitters, AFM tips etc

*2. Have you implemented the invention (e.g., made a prototype) or otherwise shown that it is workable?
● Yes ○ No

*3. Has the subject matter of the invention or a product incorporating the invention been offered for sale, or is it likely to be offered for sale, as part of an IBM product or service?
● No known product plans within 2 years
○ Maybe; GA 1-2 years away
○ Yes; GA within 3-12 months
○ Yes; GA within 3 months
○ Yes; product has been announced

*4. Has the invention been commercially used (internally or externally) by IBM or another entity (e.g., included in or used to make products, or prototypes provided to a customer)?
○ Yes ● No

*5. In what type of product might a competitor include the invention?
Logic circuits, memory, field emitters, Atomic force microscopes

What competitor(s) (indicate home country of such competitors if not United States)?
Intel, Hitachi (Japan), Motorola, Texas Instruments, TSMC (Taiwan) etc

*6. How easily can the use of the invention by a third party be detected?
○ Undiscoverable; third party must admit use for IBM to know
○ Difficult; e.g.; with reverse engineering or examination of available code
● With work; e.g.; using test cases; but not reverse engineering
○ Easily; by running & viewing product operation
○ Trivally; without purchase of product; e.g.; by reading product literature

Please propose how a test would be performed and what test methods may be required:
The Carbon Nanotubes can be easily seen in a scannining electron microscope or an atomic force microscope

*7. Is the invention applicable to a standard?
○ Yes ● No

*8. Have you, or any of the other inventors, submitted this invention disclosure or a similar invention disclosure previously?
○ Yes ● No

**9. Please list the invention disclosures (previously submitted or about to be submitted), products, patents, or publications that you and the other inventors feel are the most relevant to your invention (e.g., pertaining to the problem you are solving, including other solutions to the problem), be they from you or anyone else, or if not applicable, enter "None":
None

* 10. Was the invention made in the course of any activity that involved any other party, be it
  - The government
  - A customer (such as an RFQ)
  - A development partner
  - An alliance
  - Any contract activity
  - As part of a standards setting activity
  - Other persons not employed by IBM

  ' Yes ● No

*11. Have you ever disclosed your invention to anyone outside IBM, or do you plan to do so in the future?
' ' Yes ● No

*12. If the invention relates to a product or service that is outside the scope of your business unit, please recommend IBM business unit(s), IBM location(s) or individual(s) within IBM that you think would provide a competent evaluation of your invention:

***PVT II**

All of the questions below are required and must be answered in order to calculate a PVT Score

A.Threshold Questions

*1. **Operability** - Is there an identifiable operable embodiment of the invention (i.e., an embodiment that has been demonstrated or that would be reasonably expected to provide the benefits of the invention)?
X Yes ' ' No

Reasons for above answer:

*2. **Novelty**- Are one or more concept(s) of the invention novel over what is already known in the literature, existing commercial products, patents, and earlier IBM invention disclosures?
X Yes ' ' No
Reasons for above answer:

B.Valuation Questions

*1. Adequacy of Description:
' ' Inadequate; invention unclear from description
' ' Incomplete; essential features missing
X Further clarification or implementation detail needed
' ' Clear and complete as is
State reason for answer:

*2. Technical contribution of invention:
' ' None
' ' Minor addition to known technology
X Significant addition to known technology
' ' Major advance in technology
Reasons for above answer:

*3. Describe the problem solved/benefit provided and the implementation cost of the invention compared to existing or reasonably expected alternatives:
' ' Minor problem/incremental benefit - significant implementation cost
' ' Significant problem; substantial benefit - significant implementation cost
' ' Minor problem/incremental benefit - minor implementation cost
X Significant problem/substantial benefit - minor implementation cost

*4. Are any alternatives to the invention available to those wishing to avoid its use?
( ) Suitable alternatives available
(X) Alternatives have drawbacks
( ) No feasible alternatives
Reasons for above answer:

*5. Describe the likelihood of use of the invention (answer each):
IBM's customers? ( ) Unlikely (X) Possible ( ) Probable ( ) Definite
IBM's suppliers/vendors? ( ) Unlikely ( ) Possible (X) Probable ( ) Definite
IBM's competitors? ( ) Unlikely ( ) Possible (X) Probable ( ) Definite
IBM? ( ) Unlikely ( ) Possible (X) Probable ( ) Definite
Reasons for above answer:

*6. What % of third party products in the technical field will likely contain the invention?
( ) < 25%
(X) 25-50%
( ) 50-75%
( ) > 75%
Reasons for above answer:

*7. How long is the invention likely to be used in products by IBM or others?
( ) < 5 years
( ) 5-10 years
(X) 10-15 years
( ) > 15 years
Reasons for above answer:

*8. How easily can use of the invention by a third party be detected?
( ) Undiscoverable; third party must admit use for IBM to know
(X) Difficult; e.g.; with reverse engineering or examination of available code
( ) With work; e.g.; using test cases; but not reverse engineering
( ) Easily; by running & viewing product operation
( ) Trivially; without purchase of product; e.g.; by reading product literature
Reasons for the above answer, including description of how use could be detected:

Post Disclosure Text & Drawings
To add additional information related to this disclosure once it has been submitted, click the action button below and a new document will be opened for you to enter the new information. To view existing post disclosure information, double-click on the item in the list below (if there has been additional information entered), and the document will open for you to view.
Date entered **Post disclosure information (comments and drawings)**

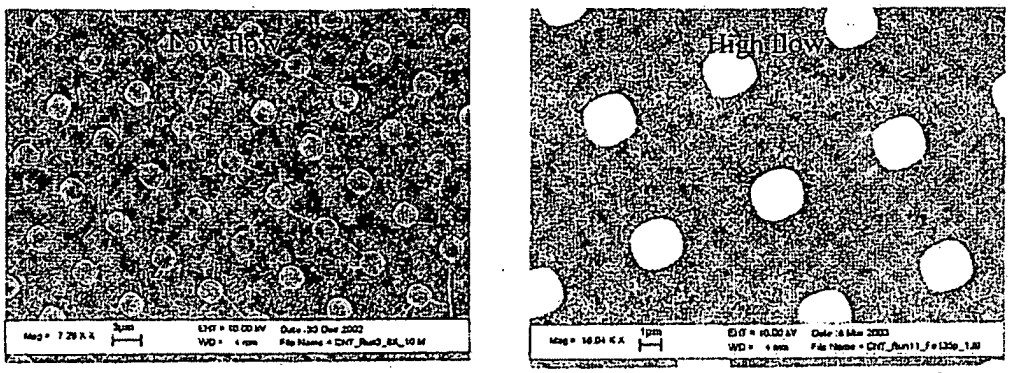

Fig. 1 Effect of gas flow on CNT diameter. For identical catalyst preparation and growth temperatures the tube diameter decreases significantly for high flows rates.

Disclosure YOR8-2003-0325

Prepared for and/or by an IBM Attorney - IBM Confidential

Created By Dinkar Singh On
Last Modified By Barbara Miuccio

Required fields are marked with the asterisk (*) and must be filled in to complete the form.

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Carbon nanotube diameter control using gas flow

Summary

Status		Final Decision (File)
Final Deadline		
Final Deadline Reason		
Docket Family		YOR9-2003-0300
*Processing Location		Yorktown
*Functional Area	select	(702F) 702F NANOSCALE MATERIALS & DEVICES
Attorney/Patent Professional		Robert M Trepp/Watson/IBM
IDT Team	select	Christopher B Murray/Watson/IBM H-S Philip Wong/Watson/IBM Robert M Trepp/Watson/IBM
Submitted Date		
*Owning Division	select	RES
Incentive Program		
Lab		
*Technology Code		101Y2
PVT Score		63

Inventors with a Blue Pages entry

Inventors: Dinkar Singh/Watson/IBM, Deborah Neumayer/Watson/IBM, Alfred Grill/Watson/IBM

Inventor Name	Inventor Serial	Div/Dept	Inventor Phone	Manager Name
> Singh, Dinkar V. (Singh)	4A8564	22/K4WC	862-3525	Grill, Alfred
Neumayer, Deborah A.	660407	22/K4WC	862-2601	Grill, Alfred
Grill, Alfred	043578	22/K4WD	862-1492	Haensch, Wilfried E.

> denotes primary contact

Inventors without a Blue Pages entry

IDT Selection

Attorney/Patent Professional	Robert M Trepp/Watson/IBM
IDT Team	Christopher B Murray/Watson/IBM H-S Philip Wong/Watson/IBM

Robert M Trepp/Watson/IBM

Response Due to IP&L

***Main Idea**

To view the main idea for this disclosure, click on this doclink ---> (If you are prompted to enter a server name, please enter D01DB016)

***Patent Value Tool**

*** 1.** Select the single most appropriate technology category for your invention from the following technologies list.
(101Y2) PPM 100 Solid State Technologies-101Y2 - Nanotechnology: devices(nanotubes, nanowires, nanoparticles etc.) and processes/materials for making these
Comments
Are there any additional significant markets where the invention is likely to have impact?
● Yes ○ No

Please identify them:
Any market involving products that use carbon nanotubes e.g. field emitters, AFM tips etc

***2.** Have you implemented the invention (e.g., made a prototype) or otherwise shown that it is workable?
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● No known product plans within 2 years
○ Maybe; GA 1-2 years away
○ Yes; GA within 3-12 months
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***5.** In what type of product might a competitor include the invention?
Logic circuits, memory, field emitters, Atomic force microscopes

What competitor(s) (indicate home country of such competitors if not United States)?
Intel, Hitachi (Japan), Motorola, Texas Instruments, TSMC (Taiwan) etc

***6.** How easily can the use of the invention by a third party be detected?
○ Undiscoverable; third party must admit use for IBM to know
○ Difficult; e.g.; with reverse engineering or examination of available code
● With work; e.g.; using test cases; but not reverse engineering
○ Easily; by running & viewing product operation
○ Trivally; without purchase of product; e.g.; by reading product literature

Please propose how a test would be performed and what test methods may be required:
The Carbon Nanotubes can be easily seen in a scannining electron microscope or an atomic force microscope

***7.** Is the invention applicable to a standard?
○ Yes ● No

***8.** Have you, or any of the other inventors, submitted this invention disclosure or a similar invention disclosure previously?

○ Yes ● No

**9. Please list the invention disclosures (previously submitted or about to be submitted), products, patents, or publications that you and the other inventors feel are the most relevant to your invention (e.g., pertaining to the problem you are solving, including other solutions to the problem), be they from you or anyone else, or if not applicable, enter "None":
None

* 10. Was the invention made in the course of any activity that involved any other party, be it
- The government
- A customer (such as an RFQ)
- A development partner
- An alliance
- Any contract activity
- As part of a standards setting activity
- Other persons not employed by IBM

○ Yes ● No

*11. Have you ever disclosed your invention to anyone outside IBM, or do you plan to do so in the future?
○ Yes ● No

*12. If the invention relates to a product or service that is outside the scope of your business unit, please recommend IBM business unit(s), IBM location(s) or individual(s) within IBM that you think would provide a competent evaluation of your invention:

*PVT II

All of the questions below are required and must be answered in order to calculate a PVT Score

A.Threshold Questions

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Reasons for above answer:

*2. **Novelty**- Are one or more concept(s) of the invention novel over what is already known in the literature, existing commercial products, patents, and earlier IBM invention disclosures?
● Yes ○ No
Reasons for above answer:

B.Valuation Questions

*1. Adequacy of Description:
○ Inadequate; invention unclear from description
○ Incomplete; essential features missing
● Further clarification or implementation detail needed
○ Clear and complete as is
State reason for answer:

*2. Technical contribution of invention:
○ None
○ Minor addition to known technology
● Significant addition to known technology
○ Major advance in technology
Reasons for above answer:

*3. Describe the problem solved/benefit provided and the implementation cost of the invention compared to existing or reasonably expected alternatives:
○ Minor problem/incremental benefit - significant implementation cost
○ Significant problem; substantial benefit - significant implementation cost
○ Minor problem/incremental benefit - minor implementation cost
● Significant problem/substantial benefit - minor implementation cost

*4. Are any alternatives to the invention available to those wishing to avoid its use?
○ Suitable alternatives available
● Alternatives have drawbacks
○ No feasible alternatives
Reasons for above answer:

*5. Describe the likelihood of use of the invention (answer each):
IBM's customers? ○ Unlikely ○ Possible ● Probable ○ Definite
IBM's suppliers/vendors? ○ Unlikely ○ Possible ● Probable ○ Definite
IBM's competitors? ○ Unlikely ○ Possible ● Probable ○ Definite
IBM? ○ Unlikely ● Possible ○ Probable ○ Definite
Reasons for above answer:

*6. What % of third party products in the technical field will likely contain the invention?
○ < 25%
● 25-50%
○ 50-75%
○ > 75%
Reasons for above answer:

*7. How long is the invention likely to be used in products by IBM or others?
○ < 5 years
● 5-10 years
○ 10-15 years
○ > 15 years
Reasons for above answer:

*8. How easily can use of the invention by a third party be detected?
○ Undiscoverable; third party must admit use for IBM to know
○ Difficult; e.g.; with reverse engineering or examination of available code
● With work; e.g.; using test cases; but not reverse engineering
○ Easily; by running & viewing product operation
○ Trivially; without purchase of product; e.g.; by reading product literature
Reasons for the above answer, including description of how use could be detected:

Evaluation

Final Evaluation History	Who made the final evaluation	Final evaluation date
Attorney Review	Christopher B Murray/Watson/IBM	

Final Decision

This decision was entered by **Barbara Miuccio/Armonk/IBM** on **06/30/2003**

Decision: File	Status: N/A

PPM Area: 100 - Solid State Technologies	Attorney Rating: 1
Date of Final Decision :	

Additional filing information

Planned Filing date:

Filing comments:

Additional decision comments

Final Decison History

Post Disclosure Text & Drawings

To add additional information related to this disclosure once it has been submitted, click the action button below and a new document will be opened for you to enter the new information. To view existing post disclosure information, double-click on the item in the list below (if there has been additional information entered), and the document will open for you to view.

Date entered	Post disclosure information (comments and drawings)

Form Revised 09/01/02)

Exhibit C

Control of Carbon Nanotube Diameter Using CVD Growth

Docket number:
List of Inventors: D. V. Singh, D. Neumayer, A. Grill

Technical field

The present invention relates to carbon nanotube growth using chemical vapor deposition (CVD), and more specifically to the control of carbon nanotube diameter during CVDgrowth.

Prior Art

Carbon nanotube based field effect transistors (CNTFETs) show great promise for device applications. Recently CNTFETs with excellent electrical characteristics comparable to state-of-the-art Si MOSFETs have been demonstrated [see, for example, S. Rosenblatt et al., "High performance electrolyte-gates carbon nanotube transistors", *NanoLetters*, 2(8), (2002) pp. 869-72]. The electrical characteristics of CNTFETs however depends strongly on the band-gap of the single wall carbon nanotube (SWNT) forming the channel of the transistor. Since the band-gap of SWNTs has a strong dependence on the diameter, accurate control of the diameter is essential to the success of any device technology based on carbon nanotubes.

A widely used technique for the growth of SWNTs with a narrow diameter distribution is based on the laser ablation of a graphite target. However controlled placement and orientation of tubes produced by laser ablation has proved extremely challenging, and limits the usefulness of this technique for circuit applications. A more attractive approach for circuit integration is to grow the carbon nanotubes in place on a suitable substrate using chemical vapor deposition (CVD). Various studies have shown the feasibility of controlling the orientation and origin of CVD grown carbon nanotubes using substrates with patterned catalyst [see, for example, S. Huang et al., "Growth of millimeter-long and horizontally aligned single-walled carbon nanotubes on flat substrates", *J. American Chemical Soc.*, 125 (2003) pp. 5636-5637].

A crucial difficulty in obtaining individual SWNTs by CVD is control of nanometric catalyst particle size at growth temperatures of 700-1000 °C. It has been theorized that the particle size of the growth catalyst used can define the diameter of as grown carbon nanotubes. This hypothesis has been supported by the observation that catalytic particles at the ends of CVD grown SWNT have sizes commensurate with the nanotube diameters [see, for example, Y. Li et al., "Growth of single-walled carbon nanotubes from discrete catalytic nanoparticles of various sizes", J. Physical Chemistry, 105 (2001), pp. 11424-11431]. Catalysts typically employed are transition metals, notably Fe, Mo, Co, Ni, Ti, Cr, Ru, W, Mn, Re, Rh, Pd, V or alloys thereof However the synthesis of small catalyst particles with a narrow diameter distribution is complicated and difficult to control.

Deleted:

Numerous strategies have been employed to control catalyst size and thus CNT diameters. One of the difficulties is to prevent catalyst agglomeration during growth of the CNT at elevated temperatures. One strategy has been to embed the catalyst particles in a high surface area silica or aluminosilicate matrix to which does not sinter during heating as detailed by A.M. Cassell, N.R. Franklin, T.W. Tombler, E.M. Chan, J. Han and H. Dai *J. Am. Chem. Soc. 1999, 121, 7975-7976.* Although a high yield of SWNT is obtained with the catalyst matrix, the matrix is extremely rough and nonconductive making patterning and electrical contact difficult.

Other approaches to control catalyst particle size include the preparation of dilute discrete nano particles in solution utilizing ferritin (iron storage protein) micelles, polymers or other coordinating reagents that bind the surface of the nanoparticles and prevent them from growing bigger. as described by Y. Li, W. Kim, Y. Zhang, M. Rolandi, D. Wang, H. Dai. However, the synthesis of dilute discrete nano particles in solution suffers from the difficulty of tightly controlling particle size and limiting their aggolomeration during CNT growth. Additionally, the dilute nature of the mixtures typically results in a lower SWNT yield, presumably due to the lower density of active sites. Other difficulties include the need to remove excess organic material surrounding the metal nanoparticle by pyrolysis and to reduce the oxide to activate the catalyst.

Another strategy which has an advantage in integration of SWNT devices is the preparation of catalyst from thin metal films which ball up during thermal treatment to form nanometric catalyst particles.

Another drawback of controlling the carbon nanotube diameter by catalyst particle size is the inability to define catalyst particles of sufficiently small dimensions by lithography. Sub 1nm dimensions are beyond the realm of even ebeam lithography and preclude the possibility of lithographically patterning individual catalyst particles for the growth of CNTs with small diameter. Hence the formation of catalyst particles is not a well controlled process and a serious drawback to any attempts at large scale integration. Growth of thin nanotubes (< 5nm) from large catalyst particles (> 20 nm) which can be patterned lithographically thus has numerous advantages from an integration standpoint.

One of the main challenges facing carbon nanotube based electronics is the low drive currents of present-day CNTFETs. The low drive current stems from the extremely small diameter of SWNTs, effectively resulting in a transistor with a narrow width. Using arrays of SWNTs for the channel region will increase the drive current, making CNTFET based technologies feasible. However, at the present time there are no controlled ways of forming arrays of CNTs with a well defined pitch. Thus the ability to grow arrays of SWNTs with lithographically controlled origins (limited by ebeam resolution) and small diameters (< 5nm) is crucial to the success of CNT electronics

It is therefore an object of this invention to provide a process for controlling the diameter of SWNTs using CVD growth conditions.

It is also an object of this invention to provide a process for forming SWNTs with diameters smaller than the size of the catalyst particle.

It is yet another object of this invention to provide a process for a single SWNT or an array of SWNTs having well defined diameters (smaller than the catalyst particle) and origins, where the SWNTs form the channel of a field-effect transistor.

It is a further object of this invention to describe a structure comprising a single SWNT or an array of SWNTs having well defined diameters (smaller than the catalyst paricle) and originating from lithographically patterned catalyst islands, where the SWNTs form the channel of a field-effect-transistor.

Summary of Invention

In accordance with the objects listed above, the present invention describes a method for controlling the diameter, d_{CNT}, of CVD grown CNTs based on the control of the residence time of the gases in the reactor by controlling the pressure, or the gas flow rates, or a combination of both, independent of catalyst particle size. By varying the growth pressure and flow rates of the CNT precursor gases in the CVD reactor d_{CNT} can be varied from 0.5nm to several nanometers. Controlling the carbon nanotube diameter by growth pressure and flow rate relaxes the constraints on the catalyst particle size. It is a significant advantage to be able to control the diameter using flow rates and growth pressure since it is much easier to control these parameters compared to the catalyst particle size. Thus this invention considerably simplifies catalyst preparation and ease of carbon nanotube integration for circuit applications. Catalyst systems, hitherto deemed unsuitable for SWNT growth due to (a) poor control of the catalyst particle size and (b) large catalyst particle size can now be utilized, such as catalysts embedded in an aluminosilicate matrix, or dilute discrete nanoparticles in solution, or thin films of catalyst metal films such as Fe, Mo, Co, Ni, Ti, Cr, Ru, W, Mn, Re, Rh, Pd, V or alloys thereof. Although the catalyst particle size may be relatively large we have shown that the CNT diameter can be effectively controlled by growth pressure and gas flow rates. This approach has the advantage that a variety of catalyst systems deposited by a variety of techniques such as chemical vapor depositon, chemical solution deposition, or physical vapor deposition can be utilized for CNT growth These films can be deposited through a mask or patterned using conventional lithography techniques allowing the growth of CNTs with small diameters (< 5nm) from lithographically defined catalyst islands (> 20nm in diameter). Thus using this technique one can easily grow an array of tubes in a controlled manner for FET applications where the nanotubes form the channel. Additionally this method can be used to further narrow the distribution in d_{CNT} for a catalyst system with a given distribution of catalyst particle size.

Brief description of the drawings

In the drawings

Figs. 1A – 1B show scanning electron microscope images of CNTs grown at atmospheric pressure using identical catalysts, but different gas flows. (a) Higher gas flow results in thin tubes while (b) lower gas flows result in thick tubes.

Figs. 2A – 2B illustrate the effects of growth pressure on CNT diameter. (a) shows a scanning electron micrograph of CNTs grown at 80 torr, while (b) shows an atomic force microscopy image of CNTs grown at 40 torr using identical catalysts (2nm thick Fe film) and gas flows. At 80 torr d_{CNT} is limited by the catalyst particle size while growth at 40 T results in much smaller d_{CNT} on the order of 2.5 ± 1.5 nm.

Fig. 3 Schematic representation of the cross-section of the starting substrate.

Fig. 4 Schematic representation of the cross-section of the starting substrate with a thin catalyst film

Figs. 5A – 5B show the (a) cross-sectional view and (b) plan view of the substrate with patterned catalyst islands.

Fig. 6 shows a plan view of the substrate with patterned catalyst islands after growth of carbon nanotubes.

Description of preferred embodiments

The present invention describes a method for controlling the diameter of CNTs grown by CVD using growth pressure and gas flow will now be described in detail. We have observed that the residence time, τ_r, of the carbon containing precursor in the reactor chamber has a strong influence on d_{CNT}. Shorter residence times result in tubes with smaller diameters, and d_{CNT} can be tuned by adjusting τ_r. Since τ_r is easily controlled by adjusting the total flow rate, growth pressure or both, this method greatly simplifies catalyst preparation and control of carbon nanotube diameter. The catalyst selected can be from the group of transistion metals including Fe, Mo, Co, Ni, Ti, Cr, Ru, W, Mn, Re, Rh, Pd, V or alloys thereof. Accurate size control of the catalyst particles is not required and a variety of catalyst systems deposited by a variety of techniques such as chemical vapor depositon, metal evaporation or sputtering, chemical solution deposition, or physical vapor deposition can be utilized for CNT growth. For example, catalysts may be deposited in the form of (a) thin metal films (on the order of 1-2 nm thick) which agglomerate at the growth temperature forming nanoparticles of the catalyst which are in the range of 0.5 to 50 nanometers in size (b) lithographically defined or (c) embedded into a suitable support structure such as porous alumina or silica. Any other suitable technique for achieving the required crude size control may be employed. The catalyst is then ramped up to the desired growth temperature in a suitable ambient prior to initiating carbon nanotube growth using a carbon containing precursor. Suitable carbon containing precursors include but is not limited to aliphatic hydrocarbons, aromatic hydrocarbons, carbonyls, halgonated hydrocarbons, silyated hydrocarbons, alcohols, ethers, aldehydes, ketones, acids, phenols, esters, amines, alkylnitrile, thioethers, cyanates, nitroalkyl, alkylnitrate, and/or mixtures of one or more of the above, preferably, methane, ethane, propane, butane, ethylene, acetylene, carbon monoxide, benzene, methylsilane. Other reactive gases such as hydrogen and ammonia, which play an important role in CNT growth, may also be introduced. The residence time of the carbon containing precursor is controlled by the combination of flow rate and growth pressure. By adjusting the gas flow rates and/or the growth pressure the diameter of the carbon nanotube can be controlled.

Example 1

An example of the effects of flow rate on carbon nanotube diameter is described below. The catalyst consisting of an aluminasilicate matrix impregnated with Fe/Mo nanoparticles is heated up to 900 °C in a hydrogen ambient. At 900 °C methane diluted in argon (Ar) is flowed through the reactor chamber over the catalyst. Fig. 1(a) shows a scanning electron micrograph of carbon nanotubes grown at atmospheric pressure for a methane flow rate of 900 sccm and no argon flow (corresponds to a residence time, τ_r of ~ 6.5 min). These growth conditions resulted in relatively thick carbon nanotubes with diameters on the order of 30nm. Fig. 1(b) shows a scanning electron micrograph of carbon nanotubes grown for a methane flow rate of 900 sccm and an argon flow rate of 1000 sccm (corresponds to τ_r ~ 3 min). Increasing the total flow rate resulted in a lower residence time for the methane and thinner tubes with d_{CNT} < 10 nm as determined by scanning electron microscopy. Accurate determination of the tube diameter with AFM was not possible due to the roughness of the catalyst used. Increasing the co-flow of Ar to 5000 sccm (τ_r ~ 1 min) resulted in no CNT growth. Decreasing CNT diameter with increasing flow rates indicates that d_{CNT} can be adjusted by controlling the flow rate.

Example 2

A second example demonstrates the effects of growth pressure on CNT diameter. The catalyst comprising a 2nm thick patterned film of Fe is heated up to the growth temperature of 950 °C in a hydrogen ambient. Figs. 2(a) – 2(b) illustrate the effects of growth pressure on CNT diameter. Fig. 2(a) shows a scanning electron micrograph of CNTs grown at 80 torr and methane flow of 100sccm ($\tau_r \sim 6$ min), while Fig. 2(b) shows an atomic force microscopy image of CNTs grown at 40 torr for the same methane flow rate ($\tau_r \sim 3$ min). It is evident that the lower growth pressure results in CNTs with a much smaller diameter. While $d_{CNT} = 2.5 \pm 1.5$ nm for the growth at 40 torr, the CNT diameter is much larger (on the order of 50nm) for a growth pressure of 80 torr.

From the above discussion it is clear that residence time can be used to control tube diameter from < 1nm diameters up-to 50 nm. It is also possible to produce tubes having a narrow distribution (< 1.5nm) using this technique as shown in Fig. 2(b). The ability to control tube diameter by residence time instead of catalyst particle size gives rise to some unique opportunities for device integration. A process for forming a novel structure comprising an array of CNTs forming the channel region of an FET will now be described.

This invention also describes construction of fully integrated structure using a thin metal film. Fig. 3 shows the cross-section of a suitable substrate, 10 which may be selected from the group comprising, silicon, silicon oxide, germanium, alloys of silicon and germanium, silicon carbide, III-V semiconductors, silicon nitride, quartz, sapphire, berryllium oxide, and aluminum nitride, other semiconductors, other insulators, conductors, such as metals or nitrides of metals. A thin film (0.5-30nm) of metal catalyst selected from the group of transition metals including Fe, Mo, Co, Ni, Ti, Cr, Ru, W, Mn, Re, Rh, Pd, V or alloys thereof is then deposited on the substrate using a suitable technique such as chemical vapor deposition, atomic layer deposition, chemical solution deposition, physical vapor deposition, molecular beam epitaxy, metal evaporation, sputtering, or electroplating. The catalyst is deposited by a suitable technique such as chemical vapor deposition, atomic layer deposition, chemical solution deposition, physical vapor deposition, molecular beam epitaxy, metal evaporation, sputtering, or electroplating and it may be prepared inside patterned porous structures. Fig. 4 shows a cross-section of the thin metal film 20, deposited on the substrate. The thin metal film is then patterned using any lithographic technique e.g. ebeam, optical dip-pen, micro-imprint etc. The unwanted catalyst can be removed by either a lift-off process or by etching so that the dimensions of the catalyst island are 100nm of less. Figs. 5(a) and (b) show the cross-sectional and plan view of the patterned catalyst islands 30. Carbon nanotubes, 40 with well controlled diameters are then grown on the patterned substrates using the method described above. Each catalyst island acts as the nucleation center for a CNT. The CNTs can be oriented during growth using electric fields or flow direction as has been described in the literature [see, for example, E. Joselevich, "Vectorial growth of metallic and semiconducting single-wall carbon nanotubes", *NanoLetters*, 2 (2002) pp.1137-1141]. Fig. 6 show the plan view of the final structure 50 after growth of aligned CNTs, 50. The structure, thus comprises of an array of CNTs with lithographically defined origins and well controlled diameters. The array of CNTs thus formed can be used as the channel of a CNT based FET for high drive current.

We have described and illustrated a method for controlling the diameter of carbon nanotubes by controlling the residence time in a CVD reactor through gas flow and pressure, independent of catalyst particle size. This process offers a big advantage in terms of catalyst preparation and the growth. When used in conjunction with a catalyst system with a narrow catalyst particle size, carbon nanotubes with a very narrow diameter distribution can be obtained. We have also described a method for forming a novel structure comprising an array of CNTs with well defined diameters and lithographically defined origins. This structure is suitable for forming the channel region of CNT based FETs. While the present invention has been described in an

illustrative manner, it should be understood that the terminology used is intended to be in a nature of words of description rather than of limitation. Furthermore, while the present invention has been described in terms of several preferred embodiments, it is to be appreciated that those skilled in the art will readily apply these teachings to other possible variations of the inventions. We now summarize what we claim is new, and what we desire to secure by letters patents.

Claims

1. A method for controlling the diameter of carbon nanotubes grown by chemical vapor deposition (CVD) in the range of 0.5–100 nm comprising the steps of
- introducing a catalyst coated substrate into a CVD growth reactor.
- increasing the reactor chamber temperature to a growth temperature 500-1200 °C.
- flowing reactive gases including a carbon containing precursor over the catalyst. The reactive gases may be diluted in an inert carrier gas.
- establishing a controlled pressure in the reactor
- adjusting the gas flows of the carbon containing precursor or the carrier gas to control the diameter of the carbon nanotubes.

2. A method for controlling the diameter of carbon nanotubes grown by chemical vapor deposition (CVD) in the range of 0.5-100 nm comprising the steps of
- introducing a catalyst in CVD growth reactor.
- increasing the reactor chamber temperature to the required growth temperature.
- flowing reactive gases including a carbon containing precursor over the catalyst. The reactive gases may be diluted in an inert carrier gas.
- establishing controlled gas flow rates into the reactor
- adjusting the pressure in the reactor to control the diameter of the carbon nanotubes

3. A method for controlling the diameter of carbon nanotubes grown by chemical vapor deposition (CVD) in the range of 0.5-100 nm comprising the steps of
- introducing a catalyst in CVD growth reactor.
- increasing the reactor chamber temperature to the required growth temperature.
- flowing reactive gases including a carbon containing precursor over the catalyst. The reactive gases may be diluted in an inert carrier gas.
- adjusting the gas flow rates and the growth pressure of the reactor to control diameter of the carbon nanotubes

4. The method of claims 1, 2 and 3 where the catalyst contains transition metal particles which can be selected from the group comprising including Fe, Mo, Co, Ni, Ti, Cr, Ru, W, Mn, Re, Rh, Pd, V or alloys thereofFe, Ni, Co, Mo and their alloys.

5. The method of claims 1,2 and 3 where the catalyst particle size are within the range of 0.5 nm to 100 nm.

6. The method of claims 1, 2 and 3 where the carbon containing precursor is selected from the group consisting of aliphatic hydrocarbons, aromatic hydrocarbons, carbonyls, halgonated hydrocarbons, silyated hydrocarbons, alcohols, ethers, aldehydes, ketones, acids, phenols, esters, amines, alkylnitrile, thioethers, cyanates, nitroalkyl, alkylnitrate, and/or mixtures of one or more of the above, preferably, methane, ethane, propane, butane, ethylene, acetylene, carbon monoxide, benzene.

7. The method of claims 1, 2 and 3 where the inert gas is selected from the group consisting of argon, nitrogen, or helium.

8. The method of claims 1, 2 and 3 where the flow rates and pressure are adjusted such that the residence time can be varied from 1 min to 20 min, preferably between 1-2min to 10 min. to tune the CNT diameter.

9. A structure comprising a single CNT or an array of CNTs with well controlled diameters smaller than the catalyst particle and lithographically defined origins formed by the process of
- depositing a thin film of catalyst on a substate
- lithographically patterning the thin films of catalyst
- removing unwanetd catalyst defined by the lithographic pattern
- Growing nanotubes with a well controlled diameter ranging from 0.5nm to 50nm using the methods of claims 1, 2, or 3.

10. The method of claim 9 where the catalyst belongs to the group of transition metals which can be selected from the group comprising including Fe, Mo, Co, Ni, Ti, Cr, Ru, W, Mn, Re, Rh, Pd, V or alloys thereof.

11. The method of claim 9 where the thickness of the thin film of catalyst can range from 0.5 to 20 nm.

12. The method of claim 9 where the catalyst can be patterned using ebeam, optical, micro-imprint or dip-pen lithography.

13. The method of claim 9 where the unwanted catalyst is removed by lift-off, wet etching, dry etching or sputtering.

14. An FET in which the structure of claim 9 forms the channel.

15. An integrated circuit containing one or more FETs described in claim 15.

Abstract

Described is a method for accurately controlling the diameter of carbon nanotubes grown by chemical vapor deposition independent of the catalyst size. For a given catalyst system the tube diameter can be varied from 0.5 nm to several nanometers by the gas flow rates or pressure or a combination thereof. Thus this technique is an extremely powerful method for controlling the diameter of CNTs, since it is relatively easy to vary the gas flow rates and pressure compared to developing catalyst systems with varying catalyst particle sizes. The ability to grow nanotubes with diameter smaller than the catalyst particles enables the growth of SWNTs from lithographically patterned catalysts, allowing the controlled growth of arrays of tubes with accurately defined origins. We describe such a structure and a process for realizing it.

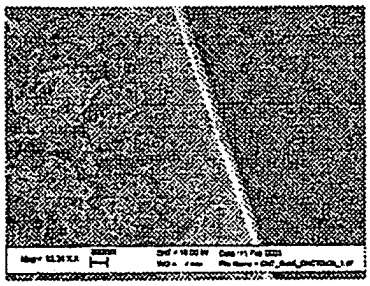

Fig 1A

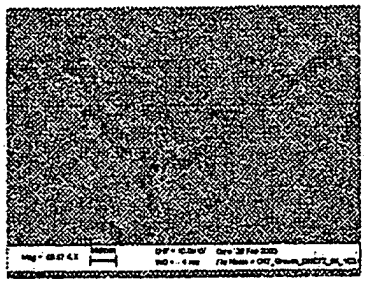

Fig 1B

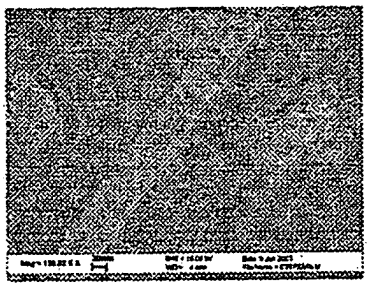

Fig. 2A

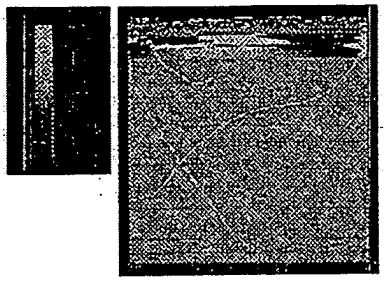

Fig. 2B

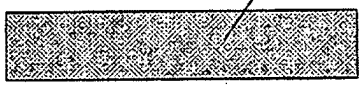

Fig. 3

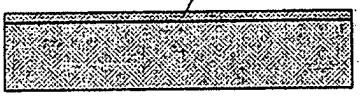

Fig. 4

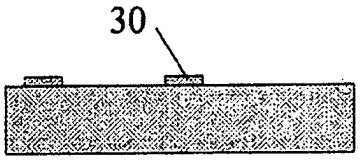

Fig. 5a

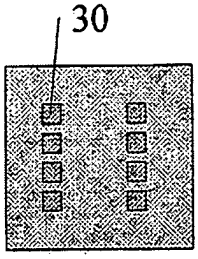

Fig. 5b

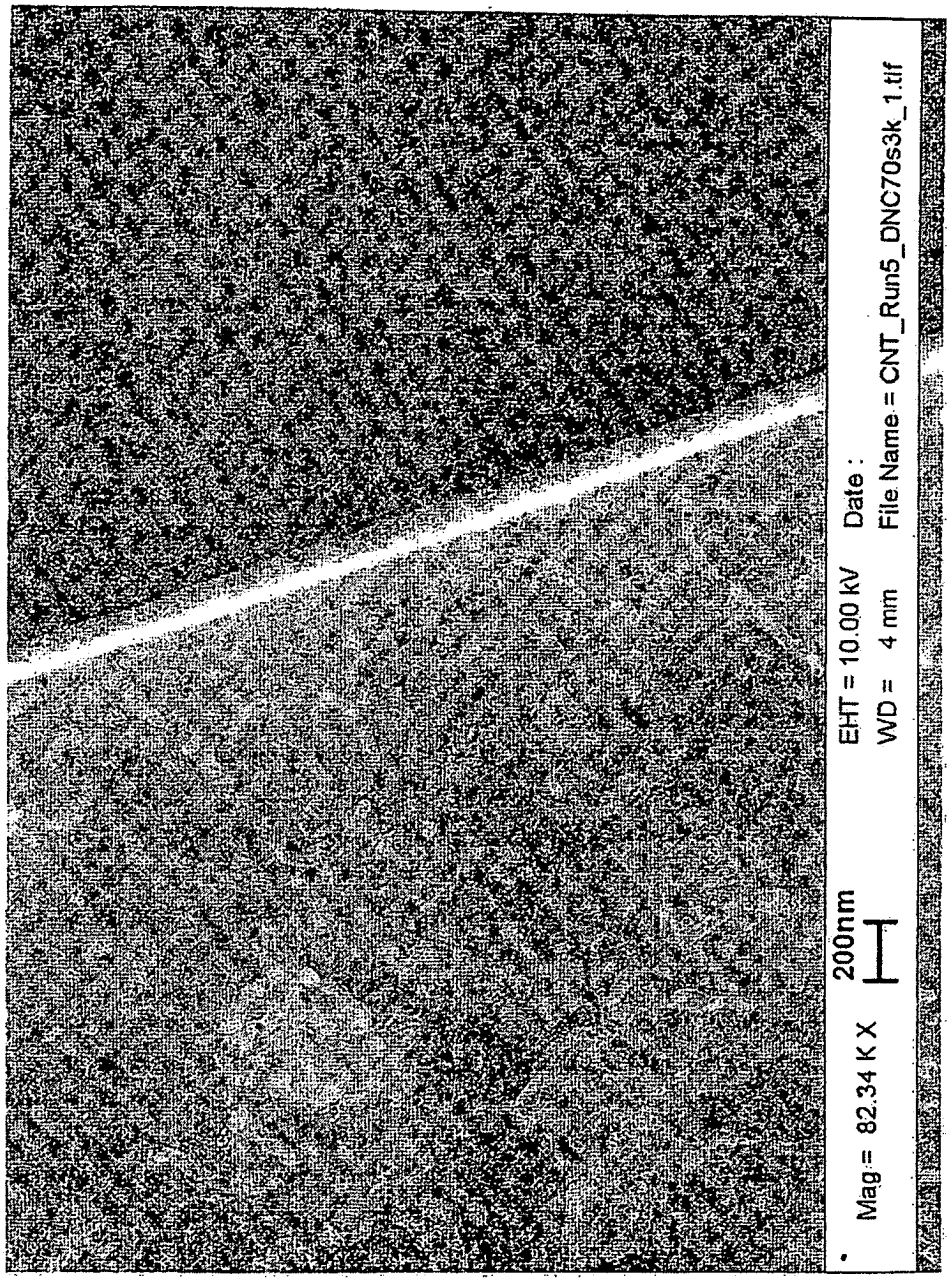
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Figure 1A

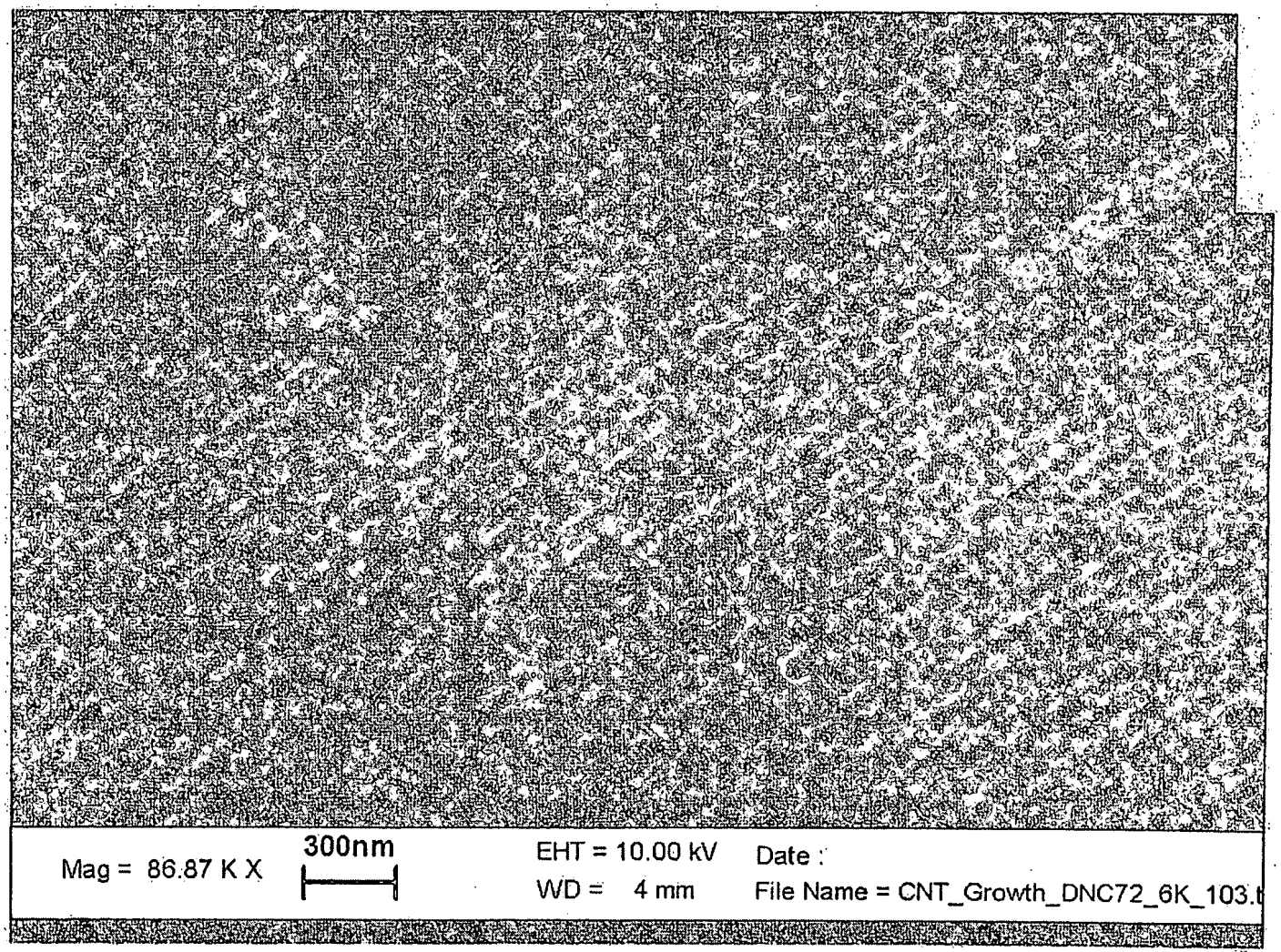

Figure 1B

Exhibit E

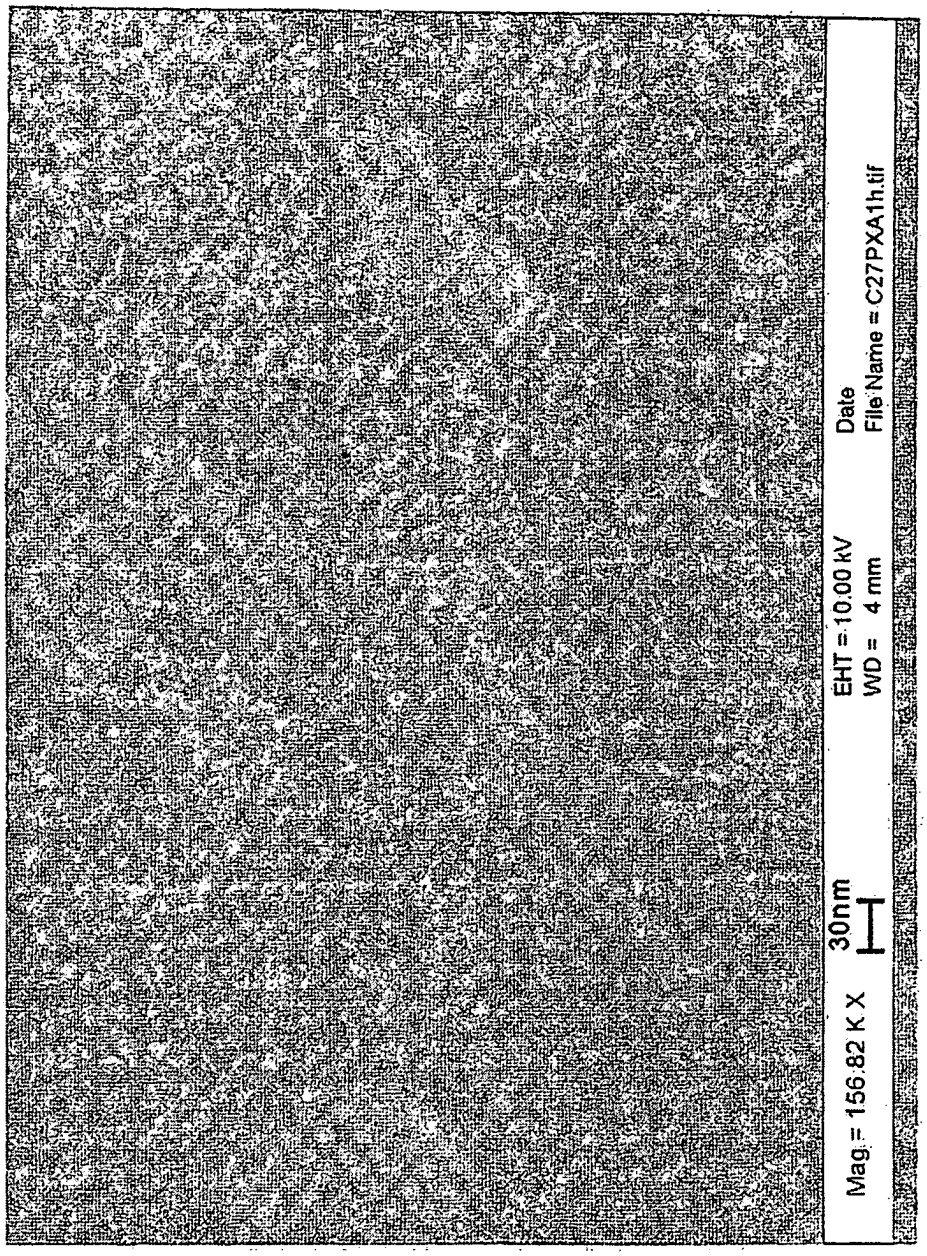
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Figure 2A

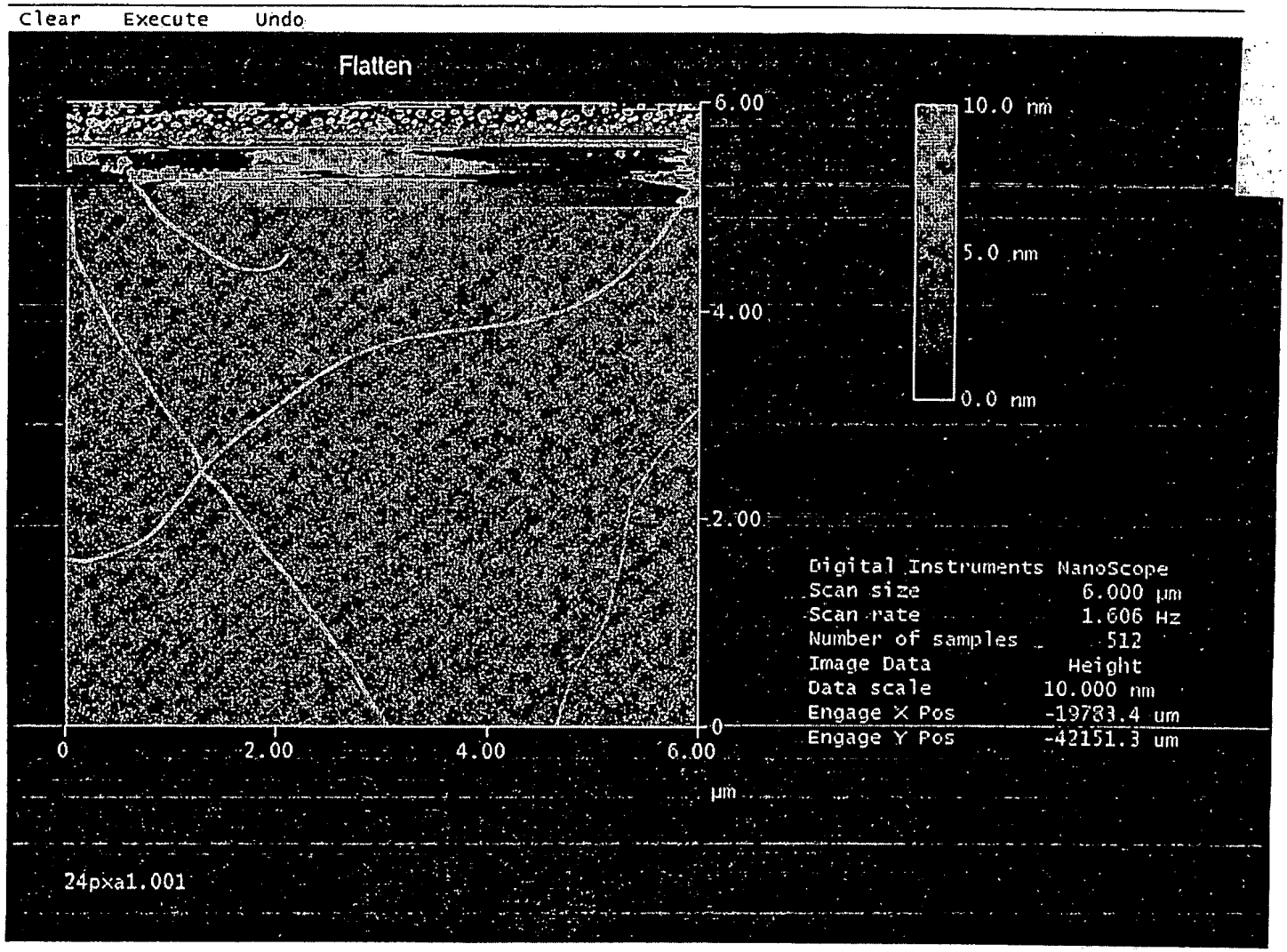

Figure 2B

Exhibit G